Control of wettability of polymers using organic surface chemistry

TIMOTHY G. BEE, ELISA M. CROSS,¹ ANTHONY J. DIAS,² KANG-WOOK LEE,³ MOLLY S. SHOICHET and THOMAS J. McCARTHY*

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003, USA

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Abstract—The analytical technique of contact angle analysis has been used both to monitor organic transformations on the surfaces of fluoropolymer films and also to help correlate surface structure with wettability. This paper describes the preparation and characterization, particularly with regard to wettability, of several series of surface-modified derivatives of chemically resistant polymers. A series of esters prepared with acid chlorides and alcohol-functionalized poly(chlorotrifluoro-ethylene) (PCTFE—OH) displays expected water contact angle trends and indicates that wettability can be controlled using organic surface chemistry. The identification of carboxylic acids on the surface of poly(vinylidene fluoride) (PVF₂—CO₂H) by the pH dependence of the water contact angle is discussed. Also described and compared with X-ray photoelectron spectroscopy is the use of contact angle for observing polymer surface reconstruction.

Keywords: Polymer surfaces; surface chemistry; wettability; fluoropolymers.

1. INTRODUCTION

Surface properties have an impact on most applications of polymer materials. We have been interested in the role that organic chemistry plays, and can play, in determining surface properties and have been carrying out research to control these surface properties using organic surface chemistry and to learn to predict surface properties with a knowledge of surface chemical structure. To this end, we have developed methods for introducing reactive organic functional groups to the surfaces of fluoropolymer films. Fluoropolymers were chosen because of their chemical resistance; to be able to correlate properties with structure, we need a series of film samples that differ *only* in their surface chemistry. After introduction of reactive functionality, the fluoropolymer films serve as inert supports and do not change upon further chemical transformations of the surface functional groups.

We have developed methods for surface functionalization of poly(tetrafluoroethylene) (PTFE) [1], poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) [2-4], poly(chlorotrifluoroethylene) (PCTFE) [4-10] and poly(vinylidene fluoride) (PVF₂) [4, 11, 12]. So far, we have focused primarily on chemistry and

^{*}To whom correspondence should be addressed.

¹ Present address: 3M Center, St. Paul, MN 55144, USA.

² Present address: Exxon Chemical Company, Baytown, TX 77520, USA.

³ Present address: IBM-T.J. Watson Research Center, Yorktown Hts, NY 10598, USA.

have done little which is directed at property correlation or property control. However, we use contact angle measurements routinely to monitor reactions. Thus, in retrospect, we can correlate wettability with surface structure. This correlation is the major focus of this paper. In addition, we will review some work on polymer surface reconstruction that uses contact angle to monitor the reconstruction.

2. EXPERIMENTAL SECTION

2.1. Materials

The syntheses of the majority of the surfaces discussed have been described [4, 6, 7]. Esters of PCTFE-OH not previously reported were prepared using the appropriate acid chloride and conditions essentially identical to those that have been reported [10]. The synthesis and characterization of the PCTFE-CO₂H samples and derivatives is reported elsewhere [13].

2.2. Methods

Contact angle measurements were obtained with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24- or 25-gauge flat-tipped needle. House distilled water which was redistilled with a Gilmont still was normally used as the probe fluid. Buffered pH solutions were prepared and adjusted to the desired pH level using a Fisher 825MP pH meter. Dynamic angles were determined by measuring the tangent of the drop at the intersection of the air/ drop/surface while adding (advancing contact angle $-\theta_A$) and withdrawing (receding contact angle $-\theta_R$) solution to and from the drop. The values reported are averages of at least five measurements taken at different locations on the film sample; individual measurements varied less than 2°. X-ray photoelectron spectra (XPS) were recorded using a Perkin Elmer-Physical Electronics 5100 spectrometer using Mg K_a excitation (300 W-achromatic) at take-off angles of 15° and 75°. Reported binding energies are not corrected for charging. Attenuated total reflectance infrared (ATR IR) spectra were obtained under nitrogen using an IBM 32 FTIR and a germanium (45°) internal reflection element.

3. RESULTS AND DISCUSSION

3.1. Esters of PCTFE-OH

Alcohols can be introduced to the surface of PCTFE by reaction with a protected alcohol—containing a lithium reagent—and subsequent deprotection equation (1). The water contact angles for virgin PCTFE are $104^{\circ}/77^{\circ}$ (θ_A/θ_R); after reaction with the protected alcohol which contains a lithium reagent, contact angles decrease to $88^{\circ}/37^{\circ}$ and after hydrolysis, decrease further to $67^{\circ}/17^{\circ}$. These changes correspond to the author's 'chemical intuition' and are supported by literature values [14]: the fluorochloropolymer surface is quite hydrophobic, the acetal is more wettable and the polar, hydrogen bonding alcohol surface (PCTFE—OH) is most wettable. The structures exhibited in equation (1) are abbreviations and are not exact; these surfaces have been

characterized in detail by XPS and ATR IR spectroscopies [7] and in fact there are ~ 4 acetal or alcohol groups every five polymer repeat units.



We can certainly make good chemical arguments to explain the wettability differences described above, but there are also physical differences in the surfaces. The three surfaces are indistinguishable by SEM at all magnifications, but smaller scale roughness differences likely exist. We have prepared a series of esters of PCTFE—OH by reaction with acid chlorides. Each of these surfaces differs only in the structure of the acid portion of the ester. Table 1 shows the water contact angle data for 10 ester surfaces. Each reaction was monitored by XPS and ATR IR; contact angles were measured on quantitatively converted surfaces. Each reaction was run in THF at room temperature. Pyridine was added as a catalyst in several cases. It is clear from the data in Table 1 that wettability is controlled by the identity of the surface functionality and that quite fine control is possible. The acetate, adipate, decanoate and stearate surfaces decrease in wettability with increasing hydrocarbon content. Likewise, the trifluoroacetate, pentafluorobenzoate, heptafluorobutyrate and perfluorodecanoate contact angles increase with increasing fluorocarbon content.

One esterification reaction (with pentafluorobenzoyl chloride) was particularly slow, and in the course of studying this reaction, we ran enough experiments to determine crude kinetics. The reaction progress of ~ 1500 Å—modified PCTFE—OH samples was monitored by contact angle, XPS and ATR IR after 12-, 24- and 48-h reactions. Each of these techniques assesses a different depth of the polymer film sample. Contact angle monitors the outer several angstroms,

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	Contact angles		
Sample	$\overline{\theta_A}$ (°)	θ_R (°)	
PCTFE	104	77	
PCTFE-OH	67	17	
PCTFE-OC(O)CH ₃	75	35	
$PCTFE-[OC(O)CH_2CH_2]_2^a$	76	43	
PCTFE-OC(O)CH ₂ CH ₂ CH ₂ CH ₃	89	51	
PCTFE-OC(O)CH ₂ (CH ₂) ₇ CH ₃	103	61	
PCTFE-OC(O)CH ₂ (CH ₂) ₁₅ CH ₃	106	78	
PCTFE-OC(O)CF ₃	92	51	
$PCTFE-OC(O)C_6F_5^b$	94	62	
PCTFE-OC(O)CF ₂ CF ₂ CF ₂ CF ₃	98	65	
PCTFE-OC(O)CF ₂ (CF ₂) ₇ CF ₃	118	69	
PCTFE-OC(O)CCl ₃	87	67	

 Table 1.

 Water contact angle data for PCTFE—OC(O)R samples

^a Prepared with adipoyl chloride.

^bPrepared with pentafluorobenzoyl chloride.

XPS (under the conditions used) indicates the composition of the outer ~40 Å and ATR IR assays the entire modified region. Table 2 shows the results of contact angle and XPS atomic concentration. Figures 1 and 2 display ATR IR and C_{1s} region photoelectron spectra, respectively. Data for the complete conversion

Reaction conditions	Contact angles		Atomic concentrations (%)		
	θ_A (°)	θ_R (°)	C	F	0
0 h	67	17	68.8	16.3	14.9
12 h	83	34	61.1	25.1	13.7
24 h	9 0	55	56.3	32.2	11.5
48 h	91	57	56.0	33.4	10.7
24 h (with pyridine)	94	62	55.6	33.8	10.6

Contact angle and XPS atomic concentration data for reactions of PCTFE-OH with pentafluorobenzoyl chloride



Figure 1. ATR IR spectra of the product film surfaces from the reactions of PCTFE—OH with pentafluorobenzoyl chloride in THF at room temperature for 0 h (a), 12 h (b), 24 h (c), 48 h (d), and 24 h in the presence of pyridine (e). Reprinted with permission from Macromolecules 1988, 21, 2318. Copyright 1988 American Chemical Society.

Table 2.



Figure 2. C_{1s} regions of XPS spectra for the product film surfaces frm the reactions of PCTFE-OH with pentafluorobenzoyl chloride in THF at room temperature for 0 h (a), 12 h (b), 24 h (c), 48 h (d), and 24 h in the presence of pyridine (e). Reprinted with permission from Macromolecules 1988, 21, 2318. Copyright 1988 American Chemical Society.

(accomplished with pyridine catalysis) are included. The results indicate that reaction occurs at approximately equal rates in each sampling region. This suggests that diffusion of pentafluorobenzoyl chloride into the modified surface is fast, relative to reaction.

3.2. $PCTFE-CO_2H$ and derivatives

Using similar chemistry as that described above to introduce alcohol functionality, carboxylic acids can be introduced to the PCTFE surface equation (2) [13]. Water contact angles for these surfaces are summarized in Table 3. The contact angles decrease from $104^{\circ}/77^{\circ}$ (for PCTFE $-\theta_{A}/\theta_{R}$) to $77^{\circ}/49^{\circ}$ for the trimethyl orthobutyrate-protected carboxylic acid surface to $55^{\circ}/0^{\circ}$ for PCTFE $-CO_{2}H$. Esterification of PCTFE $-CO_{2}H$ with n-octanol (*p*-toluenesulfonic acid catalysis) produces a hydrophobic ester surface ($\theta_{A}/\theta_{R} = 98^{\circ}/47^{\circ}$). Reduction of the acid with borane \cdot THF complex produces an alcohol surface

Table 3. Water contact angle data for PCTFE-CO₂H derivatives

	Contact angles		
Sample	$\overline{\theta_A}$ (°)	θ_{R} (°)	
PCTFE	104	77	
$PCTFE - (CH_2)_3C(OCH_3)_3$	77	49	
PCTFE-(CH ₂) ₃ CO ₂ H	55	0	
PCTFE-(CH ₂) ₃ CO ₂ Oct	98	47	
PCTFE-(CH ₂) ₄ OH	62	22	
$PCTFE - (CH_2)_4 OCOC_3 F_7$	89	47	

(one additional methylene group) similar to the PCTFE—OH surface described above. The contact angles are similar: $\theta_A/\theta_R = 62^\circ/22^\circ$ compared with $67^\circ/17^\circ$. Esterification of this alcohol surface with heptafluorobutyryl chloride produces the expected hydrophobic surface ($\theta_A/\theta_R = 89^\circ/47^\circ$). The PCTFE—CO₂H surface exhibits pH-dependent contact angles with an inflection at ~pH 8 (see below).



3.3. Convenient routes to carboxylic acid surfaces

Polymers prone to oxidation can be surface-derivatized with carboxylic acids by corona or flame treatment or by reaction with strong oxidizing agents. Carbon dioxide is produced and chain ends are functionalized with carboxylic acids. We have applied this strategy to the fluoropolymers PVF_2 , FEP and PCTFE (which are inert to strong oxidants) by first introducing an oxidizable modified surface layer (several tens of angstroms thick) and then completely removing it by oxidation with potassium chlorate/sulfuric acid. A submonolayer level of carboxylic acid groups is introduced; carboxylic acids are produced as chain termini at sites where virgin polymer and the modified layer were attached equation (3). This strategy [4] was applied to butyllithium-modified PCTFE, sodium naphthalide-reduced FEP and dehydrofluorinated PVF₂ (described here).



PVF₂ was dehydrofluorinated with aqueous tetrabutylammonium hydroxide and the modified layer (PVF₂-CH=CF-) was removed oxidatively using potassium chlorate/sulfuric acid to yield PVF_2 -CO₂H. The UV-vis and C₁, photoelectron spectra of PVF₂-CO₂H are indistinguishable from those of PVF₂. The only difference observed in the XPS spectra is the presence of a small O_{1s} line at 536 eV for PVF₂-CO₂H. XPS atomic composition indicates the presence of one carboxylic acid per 13 repeat units of PVF_2 in the outer 10 Å. The water contact angles, and in particular the pH dependence of the contact angles, however show striking differences. Figure 3 shows the pH-dependence of the advancing and receding contact angles for PVF2, PVF2-CO2H and PVF_2 -CH₂OH (prepared from PVF_2 -CO₂H with borane THF). Only the PVF₂-CO₂H sample shows pH-dependent contact angles. The surface becomes more hydrophilic when $PVF_2 - CO_2H$ ($\theta_A/\theta_B = 77^{\circ}/39^{\circ}$) is titrated to $PVF_2 - CO_2^-$ ($\theta_A / \theta_B = 68^{\circ}/25^{\circ}$). The surface carboxylic acids have pKa values ranging from ~ 5 to ~ 10 . Similar behavior is observed for the PCTFE-CO₂H surface described above [13] and for oxidized polyethylene (PE-CO₂H) [15].



Figure 3. Dependence of θ_A and θ_R on pH (buffered aqueous solutions): $\blacksquare = PVF_2$, $\blacktriangle = PVF_2$ — CH₂OH, $\blacksquare = PVF_2$ —CO₂H. Reprinted with permission from Macromolecules 1991, 24, 982. Copyright 1991 American Chemical Society.

3.4. Functionalized polymer surface reconstruction

The heterogeneous reaction of PCTFE film with 2-lithiomethyl-4,4-dimethyloxazoline (equation (4)) introduces 'trimethyloxazoline' (TMO) groups onto the film surface. When the reaction is carried out in THF at 0°C for 60 min, a -20 Å layer of PCTFE—TMO forms at the film surface. Figure 4 shows C_{1s} region photoelectron spectra for PCTFE and PCTFE—TMO. The spectrum of PCTFE exhibits one relatively high binding energy peak due to CF₂ and CFCl. Two spectra of PCTFE—TMO are shown. The 75° take-off angle spectrum (**b**) represents the composition of the outer ~40 Å of the film sample and contains two peaks. The lower binding energy peak is due to all the carbons of the PCTFE—TMO repeat unit. The presence of the high binding energy peak indicates that virgin PCTFE repeat units are present in the outer 40 Å. The



Figure 4. C_{1s} regions of XPS spectra of PCTFE (a) and PCTFE—TMO recorded at take-off angles of 75° (b) and 15° (c). Reprinted with permission from Macromolecules 1990, 23, 3916. Copyright 1990 American Chemical Society.

spectrum recorded at a 15° take-off angle (c) is representative of the outer 10 Å of the film sample and indicates that this region comprised almost entirely PCTFE—TMO repeat units. Figure 5 describes a model for this surface with the small shaded circles representing PCTFE repeat units and the large open circles representing PCTFE—TMO repeat units. Water contact angles indicate substantial changes in wettability upon conversion of PCTFE to PCTFE—TMO: for PCTFE, $\theta_A/\theta_R = 104^\circ/80^\circ$, for PCTFE—TMO, $\theta_A/\theta_R = 72^\circ/25^\circ$.



Heating PCTFE—TMO film samples above 80°C induces changes in surface structure which can be observed by both contact angle and XPS. The time dependence of the advancing contact angle (θ_A) at several temperatures is shown in Fig. 6. θ_A increases, indicating a reconstruction process that lowers the surface energy of PCTFE—TMO. The thermal reorganizations are slow, occurring over days. The 100°C data points are shaded for emphasis because we compare these data with XPS results below. A 'rapid' increase in contact angle occurs over the first ~30 h of heating at 100°C (θ_A changes form 72° to ~90°) and little further increase occurs after an additional ~200 h of heating. Apparently, a final-state structure has been reached.

XPS spectra of heated samples reflect the contact angle changes. Figure 7 shows atomic concentrations (that represent the outer 10 Å of the film sample) for each of the elements as a function of time of heating. Fluorine and chlorine

Environment



Figure 5. 2-D cross sectional model of the surface region of PCTFE-TMO. \bigcirc = PCTFE-TMO repeat unit, \bigcirc = PCTFE repeat unit. Reprinted with permission from Macromolecules 1990, 23, 3916. Copyright 1990 American Chemical Society.



Figure 6. Dependence of θ_A (water) of PCTFE-TMO on time of heating at various temperatures. Reprinted with permission from Macromolecules 1990, 23, 3916. Copyright 1990 American Chemical Society.



Figure 7. Atomic concentration and % $CF_2/CFCl$ changes for PCTFE-TMO on heating at 100°C. The data are representative of the outer 10 Å of film samples. Reprinted with permission from Macromolecules 1990, 23, 3916. Copyright 1990 American Chemical Society.

increase and carbon decreases in concentration relatively rapidly over the first ~ 30 h and then level off. The nitrogen concentration decreases and the oxygen concentration (PCTFE—TMO is air sensitive) remains the same within experimental error. Figure 7 also plots the percentage of high binding energy carbon (CF₂/CFCl) vs. time of heating. The initially absent high binding energy photoelectron line (Fig. 4c) appears in the 15° take-off angle spectrum upon heating. The data indicate that ~45% of the repeat units present in the outer 10 Å are virgin PCTFE repeat units after heating for ~30 h. Figure 8 shows a model of the reconstructed surface (compare with Fig. 5). The similar rates of contact angle and XPS changes suggest that both techniques are assessing the same molecular level processes.

Environment



Figure 8. Pictorial representation of the surface region of PCTFE-TMO after heating at 100°C. O = PCTFE-TMO repeat unit, $\bullet = PCTFE$ repeat unit. Reprinted with permission from Macro-molecules 1990, 23, 3916. Copyright 1990 American Chemical Society.

4. CONCLUSIONS

We have used contact angle analysis in the course of our research to monitor surface organic transformations and reconstruction on fluoropolymer film samples. Here we have shown, in retrospect, that contact angle analysis can also be used to help correlate surface structure with wettability. A series of esterified PCTFE—OH surfaces displays expected water contact angles. Surface carboxylic acids can be identified by the pH dependence of the water contact angle. Contact angle is useful for monitoring polymer surface reconstruction.

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